Magnetic short range order above the Curie temperature in Fe and Ni

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Abstract

We report the first results of time-dependent density functional simulations of magnetic properties of Fe and Ni at finite temperatures. They reveal the existence of local moments in Ni above the Curie temperature, coupled to strong short range order. In Fe the short range order is also present to a lesser extent but spin wave like excitations persist in both materials well above the Curie temperature in the paramagnetic state. The prevailing view of magnetic order should be reconsidered in light of these findings.

A proper description of the microscopic behavior of magnetic systems at finite temperature represents one of a few fundamental problems still existing in the theory of magnetism. While numerous model theories with different adjustable parameters lead to some description of magnets at finite temperatures, the attendant approximations significantly influence the final results. *Ab initio* methods have been used since the early 1980's; however they are limited to zero temperature and largely reproduce the Heisenberg model. As might be expected, such methods provide a good description of magnets with localized moments, but the results for itinerant magnets are rather unsatisfactory. In particular, the temperature dependence of longitudinal fluctuations and magnetic short-range order (MSRO) have always been neglected.

MSRO in itinerant magnets is the subject of a long-standing controversy. Early reports on inelastic neutron scattering experiments indicated the persistence of spin wave-like modes with relatively small wave vectors above the Curie temperature T_c in both Ni and Fe[1]. Based on these results, the local band theory was developed[2], but its assumptions are incompatible with the observed Curie-Weiss susceptibility and specific heat anomaly[3]. Since then, various experiments[4] confirm the presence of some degree of MSRO in many ferromagnets, and the present belief is that it can be very strong. However, up to now theory has failed to estimate the degree of MSRO in different magnets, owing to the formidable challenges in implementing a tractable theory for real materials.

Several quantitative theoretical methods based on the use of the calculated band structure have been developed. In many cases the *ab initio* version of the single-site coherent potential approximation (CPA) was employed. The first calculation[5] evaluates the MSRO in Fe by calculating the non-local exchange coupling. However, the single-site CPA presupposes that MSRO is absent; hence the calculated MSRO is small. Further CPA calculations[6] also obtained a good description of finite-temperature properties of bcc Fe, but do not find any local magnetic moment (LMM) at high temperatures in fcc Ni. Using Onsager's reaction-field approach[6], the description of Ni can be improved, which indicates that some interatomic correlations beyond the mean-field approximation (MFA) should be included, at least for Ni.

Different tight-binding methods not based on the CPA have been used to estimate the MSRO and the effective coupling in Fe and Ni[7]. Most did not find strong MSRO and failed to explain the corresponding experimental data. In Ref.[8] it was claimed that the effective coupling is much stronger at the Curie temperature than at $T = 0$, which makes the temperature-dependence of the exchange coupling a very important problem. However, as we will discuss below, the tight-binding approximation leads to a strong underestimation of MSRO, and hence to different physics. The first band-structure calculations of the effective exchange coupling[2] may be regarded as being in the limit which is opposite to the CPA, since the local band theory assumes strong MSRO. However, these calculations[9] yielded a much smaller degree of MSRO in contradiction with the initial assumption. This contradiction has yet to be resolved. Thus, it seems that no numerical calculations so far have explicitly shown the presence of strong MSRO in Fe or Ni based on their band structures, while the experiments clearly indicate its presence.

The second key point concerns the proper inclusion of longitudinal fluctuations in itinerant magnets at finite-temperature, which are missing in any RPA theory.

If it were not for serious challenges limiting its tractability, *ab initio* spin dynamics would be a very powerful tool to address all these issues. In Ref.[10] a combination of first principles spin dynamics with different stochastic or deterministic types of finite-temperature description was proposed. In the present paper we present an implementation that makes this technique practicable, and apply it for the first time to studies of finite-temperature behavior of ferromagnetic Fe and Ni. This approach is based on time-dependent spin density functional theory[11]. The main equation in this theory is

$$i\frac{\partial\psi}{\partial t} = \left(-\nabla^2 + V(\mathbf{r}) - \frac{1}{2}(\mathbf{B}_{xc}(\mathbf{r}) + \mathbf{B}_{ext}(\mathbf{r}))\boldsymbol{\sigma}\right)\psi. \quad (1)$$

where $V(\mathbf{r})$ is a non magnetic part of the total potential, $\mathbf{B}_{xc}(\mathbf{r})$ is the magnetic part of the exchange correlation potential and $\mathbf{B}_{ext}(\mathbf{r})$ is the external magnetic field.

Instead of considering the evolution of the non-local density matrix, one can introduce the closed system of coupled equations for the three local one electron quantities: the charge density $n_\nu(\mathbf{r},t)$, the magnetization density $\mathbf{m}_\nu(\mathbf{r},t)$, and the velocity density $\mathbf{v}_\nu(\mathbf{r},t)$. Separating the magnetization dynamics adiabatically, one can

obtain the main one-electron equation of spin dynamics

$$\frac{d\mathbf{m}_\nu}{dt} = \gamma \mathbf{m}_\nu \times \left[\mathbf{B}_\nu^{kin}(\mathbf{r},t) + \mathbf{B}_{xc}(\mathbf{r},t) + \mathbf{B}_{ext}(\mathbf{r},t)\right] \quad (2)$$

where $\mathbf{B}_\nu^{kin}(\mathbf{r}) = \boldsymbol{\nabla}\left(n_\nu \boldsymbol{\nabla}\mathbf{m}_\nu\right)/n_\nu$, $d/dt = \partial/\partial t + \mathbf{v}_\nu \boldsymbol{\nabla}$, and $\mathbf{v}_\nu$ is the velocity field for the electron liquid.

The basic assumption of the local spin density approximation (LSDA) is that the exchange-correlation potential of the homogeneous electron gas with fixed charge density n and magnetization density $\mathbf{m}$ can be applied to real external potentials. In this approximation $\mathbf{B}_{xc}(\mathbf{r}) \uparrow\uparrow \mathbf{m}(\mathbf{r})$, and hence assumes very strong exchange correlation field $\mathbf{B}_{xc}(\mathbf{r},t)$ compared to the 'kinetic' field $\mathbf{B}^{kin}(\mathbf{r},t)$ and the smallness of dynamics associated with the exchange correlation term. This important approximation assumes that correlation effects do not contribute to the spin dynamics of magnets, but attributes all of the dynamics to the kinetic term. Many static calculations of spin excitations have generally confirmed that this approximation is valid for many materials. In Ref.[12] we estimated the strength of correlation effects by calculating the contribution of non-local Coulomb correlations to the spin wave stiffness in the GW approximation. This contribution happened to be very small compared to the kinetic contribution. Below we will confirm that this approximation is quite reasonable for dynamic simulations as well.

In this paper we solve Eq.(2) by using the classical Langevin approach for finite temperatures, and employ the so-called orbital dynamics approach[10] so that each orbital can precess with its own frequency, independent of the other orbitals. In this treatment we avoid the standard adiabaticity which is assumed in the dynamic rigid spin approximation, and account for all decoherence effects properly within LSDA. This approach is similar to the linear response technique when the external field is small. However, our approach does not necessarily assume that the *perturbation* is small.

All calculations were performed within LSDA using the tight-binding linear muffin-tin orbital method. In typical calculations with 100-120 atoms per cell we used 20-30 k-points in the irreducible part of the Brillouin zone. The correct description of possible long-range magnetic order (especially at low temperatures) requires that the simulation cell contains many atoms. To avoid this numerical difficulty, we added temperature-dependent spin-spiral boundary conditions[13] that is dynamical, with its corresponding equation of motion. Similar to the static case, such combined real/reciprocal space spin dynamics allowed us to significantly reduce the number of atoms per cell in our simulations and made numerous statistical calculations possible. From the physical point of view, the simultaneous inclusion of real-space short-range modes (inside the supercell) and long-wavelength modes (between supercells) enables the description of magnetic excitations developing at different length scales, as well as their interactions, on an equal footing. As we now show, the ability to include multiple-length scales was essential to this work.

First, let us discuss static properties. In Fig.1 we show the total magnetization of Fe as a function of temperature. The results for 128-atom simulations (using dynamical spin spiral boundary conditions) for Fe are shown together with the finite-size scaling result. The finite-size scaling results were obtained using supercells of four different sizes for both Ni and Fe. The effectiveness of the dynamical spiral boundary conditions can be seen in the 128-atom simulation. The low magnetization 'tail' above T_c was reproduced in standard real space calculations (Monte Carlo simulations for the Heisenberg model) only when 7000-8000 atoms were used[14]. T_c resulting from the simulation is quite satisfactory. For Fe, nearly perfect agreement with experiment is obtained: 1070K (1023K); in Ni T_c is about 25% smaller then experiment: 470 K (623K). However, this discrepancy may be attributed to the LSDA itself: the total energy difference between fully ferromagnetic and nonmagnetic Ni is about 550K (with all parameters identical to the dynamical simulation). While this upper limit to the T_c in Ni is somewhat higher when gradient corrections are added to LSDA, we do not at present have a sufficiently accurate density functional to disentangle the LSDA contribution to the error. We only suggest that this error is connected with some on-site Coulomb correlations which are missing in LSDA at $T = 0$ K. The proper acccount of quantum corrections could significantly affect T_c as well.

The effective paramagnetic moment p_c the was extracted from the calculations of high-temperature susceptibility. These moments compared to experimental values[15] are 3.3 (3.13) and 1.75 (1.6) Bohr magnetons for Fe and Ni respectively.

To interpret these large moments we will now discuss the dynamical properties. A very unusual picture of magnetic order near T_c emerges. The crucial physical quantity which reveals a degree of short- or long-range order in magnets is the spin-spin correlation function

$$S_{ij} \sim \langle\langle \mathbf{m}_i(t)\, \mathbf{m}_j(t')\rangle\rangle\,, \quad (3)$$

where $\langle\langle ... \rangle\rangle$ indicates thermodynamic average. The short-range part of S_{ij} is strongly affected by the presence of itineracy in the magnetic system. The analysis of S_{ij} shows that the average angle between nearest neighbors' LMM is 67^0 in bcc Fe near T_c, however in fcc Ni it is just 28^0. These numbers are very stable as a function of temperature: within a temperature range of $0.95T_c$ to $1.05T_c$ their overal changes do not exceed 3-4%. The deviation from 90^0 indicates that in Fe the MSRO is relatively small (but noticeable), while in Ni it is enormous. A real-space analysis of the correlation function shows that in Ni the dynamic ordering is of the spin-spiral or domain-wall type, with a period of $\sim$14 a.u. On the other hand, in Fe nearest neighbor correlations dominate and a relatively weak superparamagnetic type MSRO is realized at T_c. Overall, the dynamic correlation function has very well defined peaks well above T_c and clearly demonstrates the persistence of the spin-wave-like perturbations in the paramagnetic state of Fe and Ni. The relatively

high energy of short-wave ferromagnons in these materials is primarily responsible for this feature.

The presence of such MSRO at T_c indicates that the nearest neighbor interactions in these materials must be larger then T_c. However, the exchange couplings in these materials are well known (see Ref.[9,16]) and corresponding numbers are somewhat lower then T_c making the existence of the strong MSRO in these materials impossible. On the other hand, starting from pioneering calculations in Ref.[9] all calculations of J_{ij} assumed a long wave approximation (LWA) which has smallness parameter $\Delta \approx J_{ij}/I$, where I is the Stoner parameter[17]. In general, this approximation is inapplicable to systems with strong interatomic interactions (as in the case of itinerant magnets). We found that the usage of the more general definition $\left(J = \chi^{-1}\right)$ leads to a much better interpretation of our results. First of all, the LWA is suitable for a relatively 'localized' system such as Fe, and the corresponding change in the nearest neighbor exchange is relatively small ($\sim$15%) but still somewhat higher than T_c. Ni represents a rather itinerant system, and any local approach (especially LWA) is expected to produce a large error. In our case, J_{01} for Ni is increased by more than 3 times relative to the LWA, clearly that the effective coupling is much larger than T_c. These results explain why the MSRO was missed in previous calculations of J_{ij} and indicate that the traditional MF approach (or any other approach which is based on the assumption of 'no short-range order') is inapplicable to itinerant systems in general, predicting very high T_c (above 1000 K in Ni). This interpretation has a qualitative character due to known violation of adiabaticity criteria in the itinerant magnets.

The MSRO allows us to provide a different interpretation of the susceptibility results as described above. The increase of the effective magnetic moment p_c in the Curie-Weiss law compared to the localized model is directly related to clustering (for example, of the superparamagnetic type) when the effective moment of the cluster is several times larger then original atomic moment. The ratio of the effective moment to the atomic moment is larger in Ni than in Fe. Our calculations also indicate that in Ni a significant contribution (15%) comes from longitudinal fluctuations. The high temperature paramagnetic state of Ni has both tangential and longitudinal modes as soft modes which are much closer to each other than at $T = 0$ K. We performed several model calculations for Ni assuming static disorder with 90^0 average angle between nearest LMM (no MSRO). For all eight random configurations studied the value of p_c was much lower (about 50-60% of our theoretical value), clearly supporting MSRO contribution to the p_c. In addition, all final self consistent states in Ni for these random configurations appeared to be non magnetic. So, we believe that strong MSRO is a necessary requirement for fcc Ni to be ferromagnetic and a similar conclusion should apply to all itinerant magnets.

Such strong MSRO can not appear only at finite temperatures; it must exist already at $T = 0$ K (as indicated by our calculations of the effective coupling). To study MSRO in more detail we performed the following model calculations at T=0 K. First, we studied the degree of localization by rotating the LMM at one site by an arbitrary angle (similar to Ref.[18] but with LWA removed). In case of the fully localized Heisenberg type of interaction one can expect that such perturbation is perfectly stable and the total energy is described by $(1 - cos\theta)$ type of behavior. Our calculation revealed completely different picture (Fig.2). In case of single site perturbation, the atomic magnetic moment in Fe disappears at approximately 120^0. Longitudinal fluctuations at this point become so important that the moment is inverted. As we mentioned above, such effects can not be described in any tight-binding type of approach. In Ni the situation is even more complicated and at $\sim 50^0$ the local moment is completely destroyed. These calculations immediately suggest that both Fe and Ni do not have a well defined LMM at finite temperature. We also found, that the LMM with opposite spin configuration in bcc Fe can be stabilized if the perturbation is extended to the first shell of neighboring atoms, providing a clear range of minimal MSRO to support such strong local perturbation. In the itinerant Ni the complete flip of LMM can not be stabilized even if the perturbation is extended to the first neigboring atoms (Fig.2). The perturbation is stabilized only when it is extended to three shells of neighbors. These calculations strongly support the idea of giant MSRO in fcc Ni and relatively small (but essential) MSRO in bcc Fe.

Another indication of itineracy (and strong MSRO) only was obtained from studies of non-magnetic configurations. We estimated the range of existence of LMM in non magnetic fcc Ni. In case when LMM exist only at one atom such fluctuation is unstable and LMM simply does not exist. However, if the LMM is fixed at its equilibrium value (0.6 μ_B) on nearest atoms, the atomic LMM is stable. According to our LSDA calculations fcc Ni at its experimental density has stable LMM of $\sim$0.6 μ_B only if it has ferromagnetic interaction with two nearest shells of atoms with the same moments. This result clearly indicates that magnetism in Ni has itinerant character. Its nature in this material is not so much in intra-atomic interactions but rather in interatomic ferromagnetic interactions with nearest neighbors. This also indicates that the standard adiabatic criterion is not applicable in Ni at finite temperatures.

Such strong MSRO also allow us to resolve a very old issue of the importance of quantum corrections for T_c and high-temperature susceptibility calculations. These corrections are traditionally small in the localized systems ($4f$ magnets), but always considered to be significant in the itinerant systems. MSRO described above also strongly suppresses quantum corrections in the case of the itinerant magnets by increasing the effective moment.

In summary, we performed *ab-initio* spin dynamic sim-

ulations at finite temperatures using time-dependent spin density functional theory. Our calculations revealed the existence of magnetic short range order at T_c in $3d$ ferromagnetic magnets Fe and Ni. This short-range order is relatively small in bcc Fe (the average angle between local magnetic moments $|\theta| \sim 70^0$), while in fcc Ni it is rather large ($|\theta| \sim 25^0$). The existence of 'distorted' spin waves above T_c significantly reduces the range of applicability of the traditional models of magnetism which are based on the idea of the spin wave disappearing at T_c, and demonstrates that more reliable models of magnetism are needed. This MSRO strongly affects all observable properties and establishes that the thermodynamics of Fe and Ni can be described in the framework of the density functional approach. We believe that MSRO is a natural property of any magnet over a very wide temperature range and is the *sine qua non* in low moment ($m < 2\mu_B$) itinerant magnets where MSRO dramatically influence thermodynamical properties. This MSRO is unique in each system and has a certain 'memory' about the ground state of that system. From the methodical point of view the successful usage of our approach clearly indicates that the kinetic energy produces the largest contribution to the dynamics of magnets at finite temperature while the exchange-correlation contribution is small.

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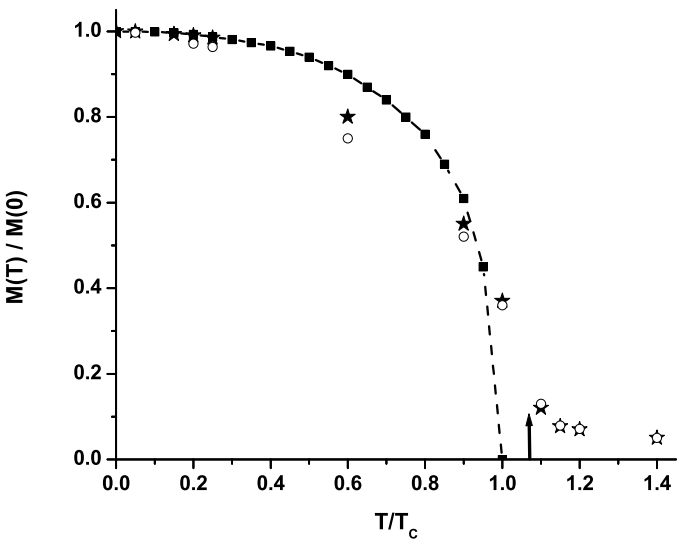
I. FIGURES CAPTIONS

Fig. 1. Magnetization of bcc Fe as a function of temperature obtained for the simulation cell containing 128 atoms with dynamic spin-spiral boundary conditions. Black stars and white circles correspond to orbital and the rigid spin approximation spin dynamics, respectively. Black squares show experimental data. The arrow indicates the finite size scaling result for the Curie temperature of Fe.

Fig. 2. Total energy as a function of angle between the magnetic moment of a single isolated impurity and the global bulk magnetization. Black circles correspond to a Ni impurity in fcc Ni; triangles, to a Fe impurity in bcc Fe; white circles, to a Ni atom with the relaxation of its nearest neighbors included. A function $(1 - cos\theta)$ is also shown by squares. The energy is normalized by the stiffness of the corresponding problem. Arrows indicate the 'critical' angles where the local moment on the given impurity disappears.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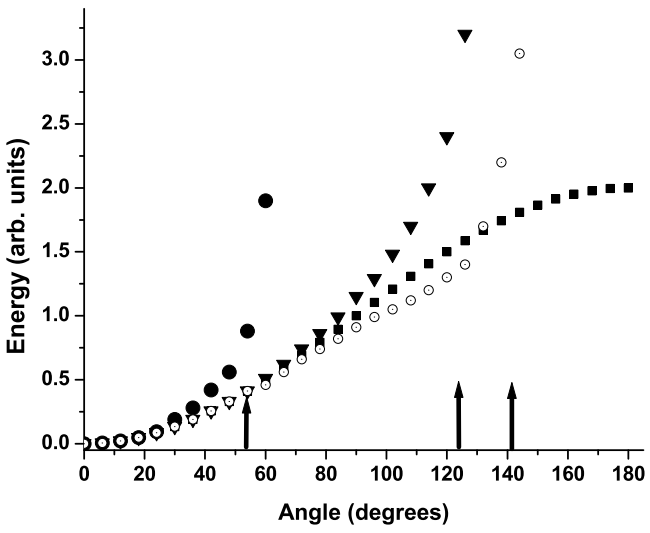
0.4
0.6
0.8
1.0
1.2
1.4


Energy (arb. units)
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2.0
1.5
1.0
0.5
0.0
0
20
40
60
80
100
120
140
160
180
Angle (degrees)